

Global Cubic Equation of State for Pure Fluids

M.Yu. Belyakov^{C, S} and E.E. Gorodetskii

Oil and Gas Research Institute, Russian Academy of Sciences, Moscow, Russia

M.A. Anisimov

Institute for Physical Science and Technology and Department of Chemical Engineering, University of Maryland, College Park, MD, U.S.A.

J.V. Sengers

Institute for Physical Science and Technology and Department of Chemical Engineering, University of Maryland, College Park, MD, U.S.A.

It is well known that any classical equation of state fails in the critical region, where the behavior of thermodynamic properties is strongly affected by density fluctuations. In the present paper we further develop a theoretical approach to account for the effects of density fluctuations in the global phase diagram of fluids. Specifically, we present an improved theoretical procedure for incorporating critical fluctuations into a cubic equation of state useful for engineering applications. The crossover equation of state contains the Ginzburg number, a parameter that controls the range of the fluctuation-induced behavior of the thermodynamic properties. Close to the critical point the fluctuations are dominant and the crossover equation reproduces Ising-like scaling behavior. Far away from the critical point the crossover equation exhibits mean-field behavior that corresponds to the original cubic equation of state. The procedure has been implemented using a Peng-Robinson equation of state. The adjustable parameters of the crossover cubic equation of state can be determined from various sets of experimental data in the one- or two-phase region. As an illustration we apply the cubic crossover equation to describe thermodynamic properties of fluids, like methane, ethane, and carbon dioxide. It is shown that incorporation of critical fluctuations leads to a significant improvement of the capability of cubic equations to represent thermodynamic properties and vapor-liquid equilibria of fluids.

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